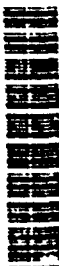


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Ion-Molecule Reactions at Very High Temperatures

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Abstract

Rate coefficients have been measured at temperatures in the range 300–1300 K for three ion-molecule reaction systems: $O^+ + NO$ and CO and $O^+ + CH_4$. These results are compared with previous studies of temperature and translational energy dependences of ion-molecule reaction rate coefficients. Problems relating to operation of a flowing afterglow apparatus at high temperatures are discussed.

1. Introduction

We have begun a study of ion-molecule reactions at temperatures unprecedented for ionic interactions. Our initial work has been in the range 300–1300 K, but the apparatus is designed for temperatures up to 2000 K. Our immediate motivation is to provide data and guidance for persons modeling high temperature plasmas (e.g. around vehicles in hypersonic flight), but it is clear that many interesting questions arise at high temperatures: new reaction channels may become activated and exotica such as "entropy-driven" reactions [1] become more accessible for study. Further, the apparatus may, in principle, be employed for measurements on electron attachment, electron-ion recombination, and ion-ion recombination. In this article we will present results on ion-molecule reactions studied thus far and will describe some of the problems encountered working at high temperatures.

A typical variable-temperature flowing afterglow or selected ion flow tube (SIFT) apparatus can operate at temperatures as high as 550–600 K using straightforward techniques, limited by the type of materials and heaters used. In the early 1970s, Lindinger *et al.* [2] modified a flowing afterglow apparatus at the National Oceanic and Atmospheric Administration (NOAA) laboratories to permit operation as high as 900 K. The NOAA group reported results for nine positive-ion reactions using this apparatus [2]. Reactions which were fast (collisional) at 300 K were found to be temperature independent within experimental uncertainty.

Reactions which were slow at 300 K were seen to decrease with increasing temperature, but in two cases a shallow minimum was observed: for $O^+ + N_2$ at 450 K, and for $CO_2^+ + O_2$ at about 700 K. (The increase in the rate coefficient at temperatures above the minimum is usually attributed to a new mechanism, such as involvement of vibrational excitation, but quantitative explanations are few.) [2] For most of the reactions studied by the NOAA group, data also existed from earlier flow-drift tube experiments. Generally speaking, the temperature variation of the reaction rate coefficients mimicked results from flow-drift tube data on the kinetic energy dependence of reaction rates. That is, for those cases where a comparison was possible, the reaction was apparently driven by translational energy and not substantially by molecular internal energy.

On the other hand, it is known that many reactions are strongly dependent upon internal excitation [3, 4]. Of primary interest to us are the effects of rotational and vibrational excitation [4, 5].

In the late 1970s, Chen *et al.* [6] constructed a static drift tube mass spectrometer capable of operation at 1500 K. Results were reported on the reactions of O^+ with O_2 for temperatures of 300–700 K, and on O^+ with N_2 for temperatures of 300–900 K. The data of Chen *et al.* agreed quite well with those from the flow-drift tube [2] and exhibited considerably less scatter than found in the flow-drift work.

We now have kinetics data on a number of positive and negative ion-molecule reactions at temperatures up to 1300 K, though the data reported here extend only to 1100 K. Our initial work has been focused on reactants which should be thermally stable (e.g. CO), but we have also looked at cases where decomposition of the reactant may be occurring, probably via surface reactions in the inlet line.

2. Experimental details

The high-temperature flowing-afterglow (HTFA) at Phillips Laboratory utilizes a 1-m long stainless steel flow tube for work up to 1300 K. The apparatus is shown in Fig. 1. The flow tube is tightly wrapped with commercial heating tapes [7] and zirconia insulation. The heating tapes can provide 4 kW of power, and have been routinely operated several hundred degrees above their rated temperature. Calculations show that the helium buffer gas comes into thermal equilibrium with the walls of the flow tube within a distance of 20 cm. The gas temperature is measured with two thermocouples located inside the flow tube along the reaction length. The thermocouples are also used as electrodes for effecting time-of-flight measurements. The upstream end of

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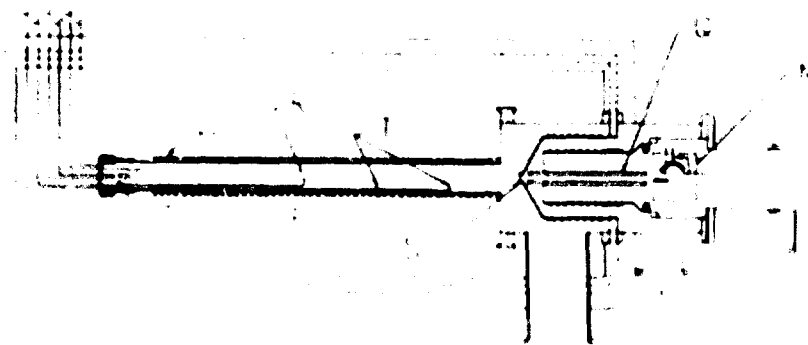


Fig. 1. A schematic of the high-temperature flowing afterglow apparatus. I: ion source; H: heating tapes and insulation; F: flow tube; R: reactant inlet; T: telescope electrodes; S: sampling aperture; Q: quadrupole mass spectrometer; M: electron multiplier; P: vacuum pumps.

the HTFA is water-cooled. The downstream end is supported by a thin stainless steel vacuum wall that is water-cooled at its circumference. The ion sampling chamber (containing lenses, mass spectrometer, and ion detector) is double-walled, with the inner chamber water-cooled.

Ions are created in the first 10 cm of the flow tube by electron bombardment of the fast-flowing helium buffer. Source gas may be added upstream or downstream of the electron bombardment zone. Reactant vapor is added at the beginning of a 63 cm reaction length. A thermal expansion correction is made to the reaction length, but amounts to only 0.95 cm or 1.5% at 1200 K. Reaction rate coefficients were determined from exponential attenuation of the primary ion intensity as the reactant concentration was increased. Details on the operation of a flowing afterglow apparatus have been given by Ferguson *et al.* [8].

We have encountered three problems. The first, a predictable problem, is loss of primary ions due to diffusion. The diffusion rate (D) increases with temperature according to a power-law dependence between T and $T^{1/2}$ depending on the ionic constituency of the plasma, for a constant pressure. Up to 1300 K, however, we have been able to overcome the diffusion dilemma with modest increases in the buffer gas flow rate (for a pressure of typically 1.3 torr at 1300 K). Also, the carrier gas velocity increases with temperature, and the shorter reaction time lessens the effect of diffusion.

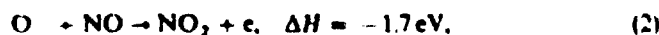
A second problem is thermionic emission of alkali metal ions from the ion sampling aperture plate (made of molybdenum), which becomes especially intense above 1000 K and precludes work with ions of certain masses above 1000 K. We replaced the molybdenum plate with a stainless steel one, which reduced the thermionic emission by a decade, but the alkali metal ion currents are still more intense than any other ion current we detect. Redesign of the electrostatic lenses (to view less of the area of the aperture plate) may mitigate this problem. The hot flow tube itself presumably emits alkali metal ions, but there is no drawout potential as in the case of the aperture plate. A Langmuir probe inside the 1200-K flow tube indicated low plasma density (an upper limit of 10^6 cm^{-3}) in absence of electron bombardment. We have detected F^+ ions due to surface-catalyzed dissociative attachment to SF_6 , and we expect that surface ionization may become a serious obstacle to work at still higher temperatures.

A final problem is thermal decomposition of reactant gas. The apparent rate coefficients for reaction of O⁺ with NH_3

and N_2O showed reasonable behavior (that is, a slow decline in agreement with flow-drift results [9] up to 750 K, but decreased precipitously at higher temperatures. The data suggest that the reactant gas was being converted into a non-reactive species. These temperatures are low enough that the decomposition must be taking place on surfaces, most plausibly in the 5-mm i.d. reactant gas inlet tube. The inlet tube is stainless steel and runs for 30 cm along the hot portion of the flow tube. The first data we obtained with the HTFA were for the fundamental nucleophilic displacement reactions $\text{Cl}^- + \text{CH}_3\text{Br} \rightarrow \text{Br}^- + \text{CH}_3\text{Cl}$ and $\text{Cl}^- + \text{CH}_3\text{I} \rightarrow \text{I}^- + \text{CH}_3\text{Cl}$, where we observed rapid rises in the apparent rate coefficients with temperatures above 700 K. Excitement over these results was quenched by a report from Pearl and Burrow [10] that a hot (>500 K) stainless-steel feedline catalyzes the formation of HCl from decomposition of CH_3Cl gas passing through it.

3. Results

Data for the associative detachment reactions,



are compared in Fig. 2 with data obtained at temperatures in the range 35–475 K in selected ion flow tube (SIFT) experiments in this laboratory [11, 12], and with rate coefficients obtained as a function of translational energy at 300 K using a flow-drift tube (FDT) apparatus at the NOAA laboratories [13]. The abscissa in Fig. 2 is given as center-of-mass kinetic energy ($3kT/2$) instead of temperature, for ease in comparison with the NOAA FDT data. Comparisons and references to earlier data sets are given in Ref. [13]. The enthalpies given with reactions (1) and (2) were calculated from thermochemical data in Ref. [14]. The calculated collisional rate coefficients for reactions (1) and (2) are 1.06×10^{-9} and $9.98 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ respectively, at 300 K. The calculations were carried out using the method of Su and Chesnavich [15] with polarizabilities and dipole moments from Ref. [14]. Since CO and NO possess small dipole moments, there is a weak decline in these collisional rate coefficients with temperature (2–3% lower at 1200 K).

A qualitative explanation for the data of Fig. 2 has been given in Ref. [13], based on resonances observed in electron scattering from CO_2 and NO_2 . The reaction efficiencies are apparently related to the fraction of potential curves for

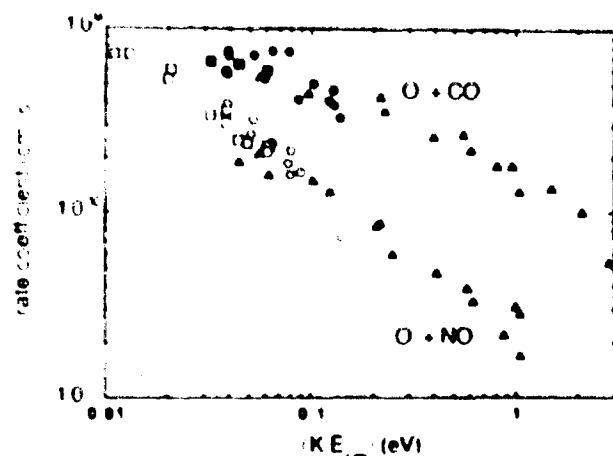


Fig. 2. Rate coefficients for reaction of O^- with CO (filled symbols) and NO (open symbols). The circles (present HTFA data) and squares (SIFT data) represent thermal measurements. The triangles (FDT data) represent data for a range of translational energies at fixed (300 K) temperature.

NO- O^- or CO- O^- that are attractive rather than repulsive. The decrease in the rate coefficients with temperature (or kinetic energy) is attributed to the shortening of the collision complex lifetime with energy. The present HTFA data (pure temperature variation) follow the trend set by the NOAA FDT data (translational energy) well, indicating that the relative translational energy is the relevant parameter controlling the associative detachment reaction. At temperatures around 1000 K the present rate coefficients tend to be lower than the NOAA data, especially for $O^- + NO$. Because of the scatter in the present data, it is not possible to be certain of a departure in the two data sets at high temperatures; results at still higher temperatures are required. The vibrational fundamentals of CO and NO are excited at only the 4–7% level at the highest temperature reached in those experiments.

Rate coefficients for the reaction



are shown in Fig. 3, compared with SIFT and FDT results. Reaction (3) is one of the best studied ion-molecule reactions [16–18]. Earlier research on this reaction is discussed in Refs [16–18]. The isomeric form of the product ion was identified by Van Doren *et al.* [16]. Barlow *et al.* [17] reacted O_2^+ with deuterated methanes to gain information on the mechanism of the insertion reaction (3). Viggiano *et al.* [18] found that excitation of low frequency vibrations in CH_4 enhances the efficiency of reaction (3) by a factor of 17. The comparison shown in Fig. 3 on the temperature dependence and the translational energy dependence of rate coefficients for this reaction is rather striking and reinforces the conclusions of Viggiano *et al.* [18]. At temperatures (400 K or 0.05 eV) where CH_4 vibrations begin to be significantly excited, the temperature dependence of the reaction rate coefficient alters course dramatically compared with the trend observed with increasing translational energy. Presumably, the C–H vibration facilitates insertion of O_2^+ into a C–H bond.

We have also obtained rate coefficients for the reaction

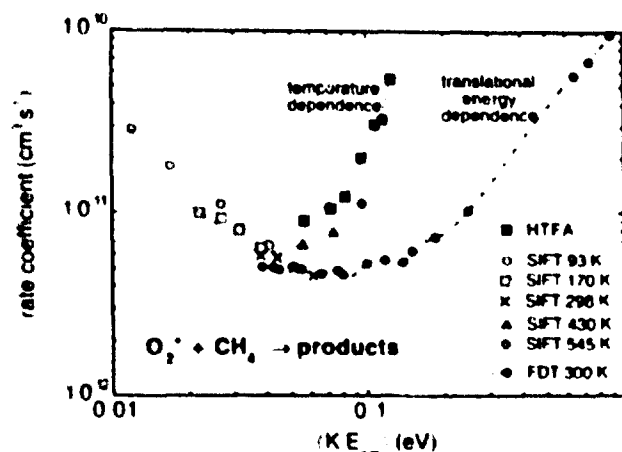


Fig. 3. Rate coefficients for reaction $O_2^+ + CH_4$. The present HTFA data correspond to thermal energies. The SIFT and FDT data correspond to a range of translational energies at the fixed temperatures indicated in the legend; the lowest-energy point of each series is a true thermal datum.

over the temperature range 300–1300 K, but we are reporting these data separately because our study of reaction (4) was integrated with a detailed theoretical analysis [19].

4. Concluding remarks

In their pioneering work on ion-molecule reactions at high temperatures, Lindinger *et al.* [2] noted that 900 K seemed "to be about the practical limit for a flowing afterglow system." Ferguson [20] also noted "This was painfully laborious. The materials problems at 900 K are horrendous, and the measured rate constants at 900 K had much larger uncertainties than the room temperature measurements."

We have constructed a flowing afterglow apparatus capable of operation at temperatures in the range 300–1300 K at present. The apparatus is being developed in three stages. The next stage will utilize a ceramic flow tube and commercial "clamshell" heating elements rated at 1600 K. The final stage will likewise make use of a ceramic flow tube, but with a commercial furnace rated at 2000 K. It is quite possible that at some point in this development program, we will find that thermionic emission and/or surface ionization or surface-catalyzed decomposition of reactants will prevent us from making measurements of rate coefficients for ion-molecule reactions above a certain temperature. The present work shows that any limitation lies above 1100 K.

We have given here results for $O^- + CO$ and $O^- + NO$ for temperatures 300–1100 K, and for $O_2^+ + CH_4$ for 300–975 K. For the two O^- reactions, the temperature dependence of the rate coefficients was the same as the translational energy dependence, with some departure possible at 1000 K. For the $O_2^+ + CH_4$ reaction, a comparison of the temperature dependence and translational energy dependence of the rate coefficients provides additional [18] evidence that CH_4 vibrations play a significant role in facilitating O_2^+ insertion into a C–H bond of methane.

In order not to be confined to using highly stable gases (e.g. N_2), we plan to experiment with a quartz reactant inlet and a cooled inlet at some point in the future. In addition, a residual gas analyzer has been installed just beyond the ion

sampling aperture plate, but only demonstration mass spectra have been obtained thus far.

One final remark: we believe that the scatter in the data presented here is not inherent to the method. The scatter is mostly related to the problem of "curvature" in the semi-logarithmic decay plot of the reactant ion current, with a number of possible explanations relating to (a) metastable helium produced in the ion source, (b) free electrons in the interaction zone, (c) incomplete production of the primary ion in the region of the flow tube ahead of the neutral reactant inlet, (d) a change in the diffusion rate in the plasma in the interaction zone, and (e) secondary reactions which regenerate the primary ion.

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References

- Meot-Ner (Mautner), M. and Smith, S. C., *J. Am. Chem. Soc.* **113**, 862 (1991); Meot-Ner (Mautner), M., *J. Phys. Chem.* **95**, 6580 (1991).
- Lindinger, W., Fehsenfeld, F. C., Schmeltekopf, A. L. and Ferguson, E. E., *J. Geophys. Res.* **79**, 4753 (1974).
- Ferguson, E. E. *et al.*, *Int. J. Mass Spectrom. Ion Processes* **117**, 261 (1992).
- Viggiano, A. A. *et al.*, *J. Chem. Phys.* **93**, 1149 (1992).
- Schmeltekopf, A. L., Ferguson, E. E. and Fehsenfeld, F. C., *J. Chem. Phys.* **48**, 2966 (1968).
- Chen, A., Johnsen, R. and Biondi, M. A., *J. Chem. Phys.* **69**, 2688 (1978).
- The heating tapes are BriskHeat Mfg. Co. model BW051080. Above 1030 K the insulation crystallizes and the tapes cannot be moved, but we have used the tapes at 1310 K without problem.
- Ferguson, E. E., Fehsenfeld, F. C. and Schmeltekopf, A. L., *Adv. At. Mol. Phys.* **5**, 1 (1969).
- Lindinger, W., Albritton, D. L., Fehsenfeld, F. C. and Ferguson, E. E., *J. Chem. Phys.* **63**, 3238 (1975).
- Pearl, D. M. and Burrow, P. D., *Chem. Phys. Lett.* **206**, 483 (1993).
- Viggiano, A. A. and Paulson, J. F., *J. Chem. Phys.* **79**, 2241 (1983).
- Viggiano, A. A., Morris, R. A., Deakyne, C. A., Dale, F. and Paulson, J. F., *J. Phys. Chem.* **94**, 8193 (1990).
- McFarland, M., Albritton, D. L., Fehsenfeld, F. C., Ferguson, E. E. and Schmeltekopf, A. L., *J. Chem. Phys.* **59**, 6629 (1973).
- "Handbook of Chemistry and Physics", 74th Edition (Edited by D. R. Lide) (Chemical Rubber Co. Press, Boca Raton 1993), 9, 42 (dipole moments); 9, 135 (bond energies); 10, 180 (electron affinities); 10, 192 (polarizabilities).
- Su, T. and Chesnavich, W. J., *J. Chem. Phys.* **76**, 5183 (1982); Su, T., *J. Chem. Phys.* **89**, 5355 (1988); **89**, 4102 (1988).
- Van Doren, J. M., Barlow, S. E., DePuy, C. H., Bierbaum, V. M., Dotan, I. and Ferguson, E. E., *J. Phys. Chem.* **90**, 2772 (1986).
- Barlow, S. E., Van Doren, J. M., DePuy, C. H., Bierbaum, V. M., Dotan, I. and Ferguson, E. E., *J. Chem. Phys.* **85**, 3851 (1986).
- Viggiano, A. A., Morris, R. A., Van Doren, J. M. and Paulson, J. F., *J. Chem. Phys.* **96**, 275 (1992).
- Viggiano, A. A. *et al.*, to be published.
- Ferguson, E. E., *J. Am. Soc. Mass Spectrom.* **3**, 479 (1992).

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